CO Oxidation Studies Over Supported Noble Metal Catalysts and Single Crystals: A Review

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SUMMARY

The catalytic oxidation of CO over noble metal catalysts is reviewed. Results obtained on supported noble metal catalysts and single crystals both at high pressures and under UHV conditions are compared. The underlying causes which result in surface instabilities and multiple steady-state oscillations are considered. In particular, the occurrence of hot spots, CO islands of reactivity, surface oxide formation and phase transformations under oscillatory conditions are discussed.

INTRODUCTION

The oxidation of CO over noble metal catalysts has been one of the most frequently studied catalytic reactions and is also perhaps the best understood of all catalytic reactions. This reaction is a problem which has attracted both the industrial and the academic sector and has fascinated catalytic chemists for many years. It is of immense importance in the control of emissions from automotive exhaust gases, enviromental cleanup and a variety of industrial applications of significant economic importance. A number of excellent reviews have recently appeared in the literature which deal with the reaction on both well-defined crystal surfaces [1,2] and on supported noble metal catalysts [3]. Of particular interest in the case of supported Pt is the occurrence of multiple steady states [4], the presence of self-sustained oscillations [3 & ref. therein], the existence of CO islands of reactivity [5,6] and induced metal and adlayer phase transitions. The importance of considering intraparticle diffusion in the case porous catalysts has been pointed out by HEGEDUS et al. [7]. More recently HERZ and MARIN [4] have shown quite convincingly that multiple steady states can arise as a result of coupling between nonequilibrium adsorption and surface kinetics.

CO oxidation studies on supported noble metal catalysts other than Pt and Pd have received less attention. CANT et al. [8] have performed CO oxidation studies on five noble metal catalysts in an attempt to bridge the gap between low pressure studies on well defined crystal surfaces and high pressure studies on supported metal powders. In these studies, the rather anomalous behavior of Ru was noted. It was suggested that the extensive catalyst deactivation might be due to the incorporation of oxygen into the Ru crystal lattice. Recently, OH and CARPENTER on the basis of an XPS study, reported that the rate of CO oxidation over Rh/Al_2O_3 was strongly dependent on the oxidation state of Rh [9].

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The current review is by no means exhaustive. However, we feel that an overview of the following areas in the catalytic oxidation of CO should serve to broaden the view of the conferees present at this meeting on pulsed CO_2 lasers: (1) reactions on supported metal catalysts, (2) reactions on selected well-defined single crystal surfaces, (3) surface instabilities and oscillatory behavior on supported noble metal catalysts at high pressures, (4) surface instabilities and oscillatory behavior on noble metals foils and under UHV conditions and, (5) surface reconstructions under UHV conditions.

REACTIONS ON SUPPORTED METALS

The catalytic oxidation of CO on supported noble metal catalysts displays a typical behavior regarding the pressure dependence of CO. The turnover frequency for the rate of CO_2 formation is plotted as a function of the ratio of the partial pressure of CO to that of O_2 in figure 1 for a 5% Ir/SiO_2 catalyst [10]. Exept for the p_{co}/p_{o_2} ratio which corresponds to the inhibition by CO, the shape of the curves is identical for all of the supported noble metal catalysts studied. At low CO/O_2 partial pressure ratios, the surface coverage of oxygen is at its maximum. Because the sticking coefficient for CO on noble metals is not a function of oxygen surface coverage, the reaction rate is controlled by the rate of CO adsorption. Following inhibition of the reaction by CO, the surface is almost completely covered by CO. In this regime, the reaction rate is controlled by the CO desorption rate and by the sticking coefficient of oxygen which is strongly dependent on the surface coverage of CO. Kinetically, in this regime, the rate can be expressed by [2]:

$$r = k\Theta_{co}\Theta_0 = k'S(O_2)p_{o_2}$$

where Θ_{co} and Θ_0 represent the fraction of the surface covered by CO and oxygen respectively, and $S(O_2)$ is the sticking coefficient for the dissociative adsorption of oxygen on the supported noble metal. It is important to note that the sum of Θ_{co} and Θ_0 does not necessarily add up to 1. The monolayer surface coverage has been shown to depend quite critically on the composition of the adlayer [11]. The *role over* region between low and high p_{co}/p_{o_2} partial pressures is characterized by rapidly changing CO and oxygen surface coverages. In this region the apparent activation energy for the reaction changes from 0 to about 100 kJ/mole and the reaction rate orders in CO and O_2 change from about +1 and -1 to -1 and +1 respectively [12]. Surface coverages of CO in both of these regimes have been substantiated by numerous *in-situ* infrared studies [10].

When the p_{co}/p_{o_2} pressure loop is reversed by increasing the partial pressure of oxygen and decreasing that of CO, a hysteresis loop develops in which the rate of CO_2 formation is observed to be considerably less than that found during increasing p_{co}/p_{o_2} partial pressure ratios [10]. A simple explanation of this observation can be rationalized on the dual site requirement for oxygen dissociation. Additionally, the sticking coefficient for oxygen dissociation is low at high surface coverages of CO. The possibility that heat transfer limitations may play a role in multiple steady—state reactions cannot be discounted. In the low CO surface coverage regime the surface may be considerably hotter than in the high CO surface coverage regime. This might be due, in part, to the higher heat of adsorption of oxygen in addition to the heat released as a result of the higher reaction rate.

The area under the hysteresis curve is a function of temperature and the particular metal under study. When the temperature is increased, the inhibition of the reaction rate is observed to occur at higher p_{CO}/p_{O_2} partial pressure ratios. This is undoubtedly due to the competitive nature of the CO and oxygen adsorption and desorption rate. At higher temperatures the desorption rate of CO increases. For this reason, higher pressures of CO are required to bring about an inhibition in the rate of reaction. Since CO is more weakly adsorbed, the lower branch of the hysteresis curve disappears due to a more facile displacement of chemisorbed oxygen by CO. CO oxidation studies on supported Pt [13] and supported Ir [10], which have about the same catalytic activity, show that at temperatures above 423 K, the hysteresis loop disappears.

CO oxidation reaction rates on supported metal catalysts should be compared at similar reactant gas phase compositions. This is of the utmost importance due to the dependence of reaction rates on the formation of strongly bound oxygen or the possible formation of subsurface oxides which may inhibit the reaction. Additionally , under oxidizing conditions, the formation of higher noble metal oxidation states may have a significant effect on catalytic activity. CO oxidation rates on Rh/SiO_2 catalysts for example [14], are inhibited by the formation of Rh(I) under net oxidizing conditions.

Reaction rates under net oxdizing, stoichiometric and net reducing reactant gas compositions at 373K are shown in table 1. Under both net reducing and stoiciometric conditions, the following catalytic sequence is observed: Ru > Ir > Pt > Rh > Pd. Under net oxidizing conditions, this sequence becomes: Rh > Ru > Pd > Ir [15]. From these results we conclude that Rh, while not a particularly active catalyst for CO oxidation, retains its activity under net reducing conditions. However, it rapidly looses its activity when exposed to oxidizing conditions [8,16].

DEACTIVATION OF SUPPORTED NOBLE METAL CATALYSTS

All supported noble metal catalysts deactivate to some extent following time on stream. Ru is the worst actor in this regard. Catalyst deactivation continues for several hours even under net reducing conditions. When a Ru/SiO_2 catalyst was exposed to a p_{CO}/p_{O_2} partial pressure of 0.25 for 12 hours, the catalyst was completely deactivated [16]. Its initial activity could only be restored following reduction in H_2 at 673 K. The buildup of unreactive oxygen, possibly in the form of unreactive chemisorbed oxygen or through the formation of a bulk subsurface oxide was offered as a reason for the observed deactivation. These results were in part confirmed using temperature programmed desorption following exposure of the catalyst to an oxygen rich reactant gas mixture for an extended period of time [16].

Catalytic CO oxidation studies on Rh/SiO_2 [14] show that Rh is quite resistant to deactivation. However, the results of a recent *in situ* infrared study show that CO oxidation rates depend to some measure on the oxidation state of Rh [9,14]. Reaction rates decrease in the following sequence: Rh(0) > Rh(I) > Rh(III). Recent studies on Ru-Rh/SiO_2 bimetallic clusters are encouraging. Evidently the formation of Ru-Rh bimetallic clusters appear to inhibit deactivation nearly completely [17].

On Pt/SiO_2, CANT et al. [18] suggest that deactivation occurs as a result of the buildup of nonreactive oxygen. To substantiate this suggestion, using *in situ* infrared methods, they observed the appearance of an unreactive infrared band centered at 2120 cm^{-1}, which he assigned to CO adsorbed on an oxidized Pt surface site. Because the decline in the catalytic activity appears to be concomittant with the appearance of this

infrared band, it can be concluded that all Pt surface sites capable of chemisorbing oxygen are not equally reactive in the oxidation of CO. In fact, because the dissociation of O_2 occurs preferentially on edges, steps and centers of low surface coordination, the blockage of these sites by unreactive chemisorbed oxygen would, in all likelihood, result in an overall decrease in the catalytic activity.

SUPPORT AND PARTICLE SIZE EFECTS

There has not been widespread agreement with respect to the effect of particle size on the rate of CO oxidation and the subject is quite controversial. SARKANY and GONZALEZ support the view that the oxidation of CO is a facile reaction on Pt/SiO$_2$ [19]. CO_2 turnover numbers measured at 373 K were insensitive to an overall increase in the Pt dispersion by a factor of 4. On Pt/Al$_2$O$_3$ the situation was not clean cut [19]. When Pt dispersions were increased from 0.17 to 0.90, the reaction rate increased by a factor of 3. Because CO oxidation results performed on Rh and Ru single crystals [20] are in excellent agreement with studies performed on supported Rh [14] and Ru [16] it appears that the reaction is, in fact, facile. In a recent CO oxidation study on supported Pd, BOUDART and ICHIKAWA [21] reported that reaction rates appeared to be faster on small particles. However, they also reported that because small particles were considerably more active in promoting the BOUDOUARD reaction, an additional route to CO_2 formation through dissociated carbon was possible. When a correction for this observation was made, they concluded that the reaction on supported Pd was facile.

Recent studies on Pt/SnO$_2$ have shown this catalyst to have a very high low temperature activity [22]. This property makes it useful for use in applications of pulsed CO_2 lasers. In a pulsed CO_2 laser, CO_2 is decomposed to CO and O_2. Because it is necessary to maintain a constant CO_2 pressure, a catalytic recycle system is necessary to reoxidize CO back to CO_2. Unfortunately, the SnO$_2$ support exchanges oxygen with CO_2 [23] and, therefore, does not maintain the isotopic integrity of the CO_2 which requires labeling with ^{18}O. This results in the instability of the lasing frequency.

REACTIONS ON SINGLE CRYSTALS

Because of the facile nature of the catalytic oxidation of CO it is of interest to compare studies on single crystal surfaces to similar studies on supported metals. In a survey study, similar activation energies (~100 kJ/mole) and kinetic orders (+1 in O_2 and -1 in CO) were found for supported Pd, Rh [15] and Ir [10] catalysts. For Ru, the situation appears to be more complex. Furthermore, Ru has been reported to be the most active catalyst for the series of supported noble metal catalysts [15] while under UHV conditions it is the least active [20].

In a recent surface science study performed under more realistic pressure conditions, GOODMAN and PEDEN [20] and OH et al. [24], have reexamined the catalytic oxidation of CO on Ru(0001) and Rh(111). In these studies, the reactor could be withdrawn from the high pressure reaction system at any time and examined using UHV methods.

Turnover frequencies for CO_2 formation on Rh(111) and Rh(100) as a function of temperature are shown in figure 2. They are in exellent agreement with similar rates obtained on highly dispersed Rh/Al$_2$O$_3$ catalyst [25]. Apparent activation energies of 121 kJ/mole were obtained on Rh(111) compared to 125 kJ/mole on Rh/Al$_2$O$_3$. A similar

agreement was obtained in studies performed on Ru(0001) and Ru/SiO$_2$ [20]. Apparent activation energies of 83.6 kJ/mole on Ru(0001) compare favorably with those obtained on Ru/SiO$_2$ (94.05 kJ/mole) [16]. Furthermore, Ru(0001) was considerably more active than Rh(111) in agreement with studies on supported metal catalysts.

The dependence of the rate of CO oxidation on the partial pressure of CO on Rh(111) decreases linearly with with increasing partial pressure of CO, figure 3 [20]. The behavior of Ru(0001) is considerably more complex. However, it too is in excellent agreement with results obtained on Ru/SiO$_2$ [16]. At low partial pressures of CO, the reaction is positive order in O$_2$.

The dependence of the CO oxidation rate on the partial pressure of oxygen on Rh(111) increases until a partial pressure ratio p_{O_2}/p_{CO} of about 30 is reached [20]. The rate roles over and is inhibited by a further increase in the partial pressure of O$_2$. These results are in good agreement with similar studies on NAFION supported Rh catalysts [25]. Perhaps a catalyticly inactive Rh surface oxide is formed at sufficiently high partial pressures of oxygen. Surface analysis of the oxygen adlayer using Auger Electron Spectroscopy (AES) showed that the role over in the reaction rate occurred following the formation of a monolayer of oxygen on Rh(111) [20]. Presumably this oxygen, whatever its nature, deactivates the catalyst.

Similar experiments on Ru(0001) [20] show that when a monolayer of oxygen is obtained, the reaction rate reaches its maximum value and becomes zero order in the partial pressure of O$_2$. This result is in striking variance to studies on Ru/SiO$_2$ [16]. For the case of supported Ru catalysts the reaction rate is strongly inhibeted by excess O$_2$. Surface AES studies show that the maximum rate of CO oxidation on Ru(0001) coincides with the maximum concentration of surface oxygen [20]. Thus, in this respect, there appears to be a significant difference in the results of the Ru single crystal studies and the supported Ru studies. Further work is needed to resolve this apparent inconsistency.

In conclusion, similar activity trends are obtained on single crystals and on supported noble metal catalysts. However, important differences also exist with respect to the dependence of the rate on the partial pressure of the reactants.

REACTIONS IN MOLECULAR BEAMS

Recent studies using molecular beams focused onto Pt(111) single crystals [26] and Pt foils [27] have led to a significant understanding of the nature of the adsorbed transition state complex which leads to the formation of gas phase CO$_2$.

When the reaction was run using a mixed molecular beam consisting of CO and O$_2$ molecules under steady state conditions [27], the infrared emission spectra of the resulting CO$_2$ product molecules showed that there vibrational frequencies corresponded to temperatures which were considerably higher than that of the surface. When the composition of the beam had excess oxygen [28], the vibrational temperature of CO$_2$ was considerably higher than that observed in a CO rich molecular beam. Perhaps, as noted earlier, the higher heat of adsorption of oxygen might result in higher surface temperatures on an oxygen covered surface.

The results of a pulsed CO molecular beam in the presence of a constant pressure of oxygen showed that the vibrational temperature was a function of oxygen surface coverage [28]. The vibrational temperature of the product CO$_2$ molecules was observed to decrease with decreasing oxygen surface coverage. Because the rotational temperature

decreased at a much faster rate than the vibrational temperature, it was concluded that the product CO_2 molecules were vibrationally excited. It would appear that a transition state with a CO_2 molecule oriented perpendicular to the surface would account for this observation. In all likelihood the excess vibrational energy is stored in the asymmetric stretching mode of CO_2.

NAGAI et al., have recently made similar observations in a transient CO oxidation study over a Pt/SiO_2 catalyst [29]. Using an *in situ* infrared cell reactor, these authors observed that the antisymmetric stretching vibration of CO_2 was red shifted by 10 cm^{-1}. Additionally the P-branch and the R-branch in the resulting transient infrared spectra could not be resolved suggesting vibrationally exited CO_2. In these studies, a pulse of CO was added to a Pt surface covered by oxygen. The resulting transient response giving rise to the infrared spectrum of CO_2 lasted for about 10 seconds during which time 10 scans were made. Future studies will be aimed at fitting the resultant transient response data of CO_2, preferably in the emission mode, to vibrational and surface temperatures.

SURFACE INSTABILITIES AND SELF-SUSTAINED OSCILLATIONS

Supported metals

Given a set of time-dependent differential equations, multiplicity is obtained when there is more than one stable, physically realizable solution to the steady-state form of the equations for a given set of parameters [3]. This characteristic is rather easily obtained for mathematical models if heat and mass transfer influences are considered. However, the underlining cause which leads to oscillatory behavior has not as yet been unambiguously determined.

Even though self-sustained oscillations during the oxidation of CO have been the most widely studied, reaction rate instabilities are by no means limited to this reaction. Self-sustained oscillations have been observed for a wide variety of surface catalyzed reactions which include: H_2+O_2, NH_3+O_2, $C_2H_4+O_2$, $CO+NO$, CH_3OH+O_2, $NO+NH_3$ and $C_6H_{12}+O_2$ [3]. It is noteworthy that most of these reactions are highly exothermic in nature and generally involve catalytic oxidations. However, several cases of reaction rate instabilities which involve reductions have also been reported [3]. For the purposes of discussion, we will limit ourselves here only to a consideration of self-sustained oscillations observed during the oxidation of CO.

The various kinetic regimes during the oxidation of CO are summarized in figure 4. In region (I) the reaction rate is controlled by the rate of CO adsorption [13]. The reaction rate in this regime is approximately first order in CO and zero order in oxygen. Under these conditions, the fraction of the surface covered by oxygen is at its maximum and the apparent activation energy is close to zero. In region (III), the reaction rate is strongly inhibited by adsorbed CO. Under these conditions, the apparent activation energy is close to 100 kJ/mole on most noble metals and the reaction rate is approximately first order in oxygen and negative first order in the partial pressure of CO.

The existence of self-sustained oscillations is limited to region (II). In this region, surface coverage of CO and oxygen vary over the pressure domain in which the oscillations occur. Apparent activation energies also change sharply as the partial pressure of CO is increased. The amplitude of the oscillations are a function of both the

partial pressure of CO and temperature [13]. This behavior is outlined in figure 5 for a Pt/SiO$_2$ catalyst. As the temperature is increased from 488 K to 544 K, the amplitude of the oscillations is observed to decrease. The dependence of the ampliutude of the oscillations on the CO partial pressure is also shown in figure 6. This amplitude increases until the surface is predominantly covered by CO and the reaction rate is rapidly quenched. The dependence of the oscillatory period on the partial pressure of CO is shown in figure 6. As the partial pressure of CO is increased, the frequency of the oscillations is observed to decrease.

A recent *in situ* infrared study by KAUL and WOLF [30] shows that these self-sustained oscillations are accompanied by large surface temperature fluctuations. A summary of their results on Pt/SiO$_2$ is shown in figure 7. Surface temperature fluctuations of up to 100 K are observed during these oscillations. Of interest in their results is that the rate of CO$_2$ production and the surface temperature do not oscillate in phase. This apparent inconsistency was resolved by inserting a second thermocouple on the surface at a location which was remote from the first. Because both thermocouples reported temperatures which differed by as much as 100 K, they concluded that hot spots were formed throughout the pressed catalyst pellet. When the temperature fluctuations were integrated over the entire surface of the catalyst pellet, the rate of CO$_2$ production, the surface oxygen coverage and the surface temperature oscillated in phase.

The occurrence of hot spots has elegantly been demonstrated by SCHMITZ and co-workers [31] using infrared thermograms. These authors observed temperature inhomogeneities during the oxidation of H$_2$ and CO over a series of Pt/Al$_2$O$_3$ catalysts.

Apparently, the relatively non-conducting support inhibits heat transfer between various locations on the catalyst bed. The reason underlying the formation of hot spots is not entirely clear. Reactor design appears to be an important variable and the occurrence of local gas phase concentration fluctuations has been offered as a possible reason for the fluctuating hot spots. Whether the oscillations are thermally or kinetically driven is a matter which is still open to debate. In order for self-sustained oscillations to occur, there must be an autocatalytic and an inhibition step. It would seem to us that these requirements should be intimately linked to changes which occur in the surface mechanism. If this were not the case, all exothermic catalytic reactions would oscillate given the right set of conditions. This is most certainly not the case.

The formation of CO islands and centers of reactivity has also been suggested as a possible mechanism which can lead to self-sustained oscillations [5,6]. This possibility is nicely illustrated in a recent *in situ* FTIR study by BÖCKER and WICKE on Pd/TiO$_2$ [6,32]. The catalytic reaction cycle which incorporates both an autocatalytic and an inhibition step is shown in figure 8. Initially, figure 8a, the surface is covered by oxygen in a (2x2) adsorbate layer configuration. Small isolated patches of CO give rise to a single wide CO infrared band centered at 1900 cm^{-1}. This vibration is due to CO adsorbed in a bridging configuration with each CO coordinated to about three surface Pd atoms. This assignment is due to the recent EELS work of BRADSHAW and HOFFMAN [33,34]. As the CO islands grow in size, the reaction rate increases to a maximum as shown in figure 8b. Because the reaction occurs at the perimeter of these CO islands, the reaction rate decreases as the CO islands increase in size. By forming these CO islands an increasing number of surface sites are lost to the reaction due to the inability of oxygen to adsorbe inside an organized CO surface structure. Concomitant with this increase in CO island size a second sharp absorption band centered at 1980 cm^{-1} is observed in the infrared spectrum of CO. This band has been assigned by

BRADSHAW and HOFFMAN [34] to CO coordinated to two Pd surface atoms. This surface species can be related to the adsorbate phase changes occurring during the CO island formation. A further increase in CO island size leads to a compression of surface oxygen into a more dense ($\sqrt{3}$x$\sqrt{3}$) adlayer structure. Because this surface oxygen which has undergone a phase transition of sorts has been shown to be considerably more reactive than oxygen adsorbed in a (2x2) adlayer configuration [1], the reaction rate again increases thus completing the reaction cycle. It appears, therefore, that surface phase transformations could lead to self-sustained oscillations.

Recent CO oxidation results in our laboratory [10] on highly dispersed Ir/SiO$_2$ (66%)have also shown the occurrence of self-sustained oscillations. Because small metal particles are unlikely to support large CO islands of reactivity it appears that different mechanisms may be responsible for the self-sustained oscillatory behavior during CO oxidation Additionally, recent studies on the CO adsorption of CO and NO [35] show that the resulting adlayers are intimately mixed. Because this reaction also oscillates [36], it is unlikely that the concept of CO islands of reactivity can be applied to this reaction.

Recent *in situ* infrared studies on Pt/Al$_2$O$_3$ [37] and Ru/SiO$_2$ [16] have also shown oscillatory behavior during CO oxidation. In these studies the formation and disappearance of reducible surface oxides were cited as possible causes for oscillatory behavior. A weakness in the concept of reducible surface oxides is that there is no built in autocatalytic and inhibitory step in the mechanism.

From the above discussion several possibilities for oscillatory behavior have been suggested. However, it is also clear that a mechanism capable of explaining all of these observations has not yet emerged. Any realistic mechanism which attempts to explain oscillatory behavior should at a minimum have built into it an accelerating autocatalytic step in addition to an inhibitory step.

Reaction on single crystals under UHV conditions

Reaction rate instabilities and self-sustained oscillations have also been observed by several workers on single crystals under UHV conditions [1,38,39]. The oscillatory behavior of the CO oxidation reaction has recently been related to phase tranformations of both the metal and the adsorbate phase [40]. (100) crystalographic planes of Au, Pt, Ir, V, Cr, Mo and W have been shown to reconstruct under the influence of both CO and oxygen adsorption [ref. in 41]. The (110) planes of Pt and Ir do not reconstruct and do not exhibit oscillatory behavior during CO oxidation.

At low CO surface coverages the Pt(100) surface exhibit a reconstructed hexagonal (5x20) surface [40]. When the CO surface coverage is increased to about half of a monolayer, a surface phase transition to an unreconstructed (1x1) surface occurs. Using a novel scanning LEED technique, ERTL has followed CO oscillatory behavior while monitoring both the metal reconstruction and the phase transformation of the CO and oxygen adlayer. The reconstructed (5x20) structure can be correlated with a high CO oxidation activity, while the unreconstructed (1x1) structure has a low CO oxidation activity. During the low point in the reaction rate, the CO adsorbate layer consists of patches of CO adsorbed in a (2x2) surface adlayer.

Changes in the sticking coefficient of oxygen following phase transition to the unreconstructed (5x20) structure may also play an important part in the acceleration of the reaction rate. Sticking coefficients for the dissociative adsorption of oxygen have

been shown to be orders of magnitude larger on the unreconstructed (5x20) structure than on the reconstructed (1x1) structure [42]. ERTL et al. [40] have shown that the onset of oscillations obtained experimentally as a function of temperature agree well with the predicted reconstruction of the metal surface.

Several attempts have been made to extend the UHV results to high pressure oscillatory behavior on supported metal catalysts. However, the point should be made that these attempts are invalid because under high CO and oxygen partial pressures, the metal surface must always be present as an unreconstructed (1x1) structure.

CONCLUDING REMARKS

The results of numerous studies allow us to conclude the following regarding the catalytic oxidation of CO over supported noble metal catalysts: (1) The catalytic oxidation of CO over noble metal catalysts appears to be a facile reaction. However, support effects, particularly SnO_2, cannot be completely overlooked. (2) Reaction rates over single crystals agree favorably with results over supported metal catalysts. (3) The occurrence of self-sustained oscillations has been observed by a large number of workers. However a single mechanism which accounts for all of the experimental observations has yet to emerge. Causes of self-sustained oscillations may include: (1) the formation of CO islands combined with a compression of the remaining oxygen adlayer structure, (2) hot spots caused by fluctuations in gas phase concentrations, (3) the formation and disappearance of reducible surface oxides, (4) heat and mass transfer effects and (5) surface phase transformations. CO oxidation studies under UHV conditions unequivocally relate phase transformations to oscillatory behavior.

In summary, much has been accomplished. However, inconsistencies reported between different laboratories abound in the literature. Further experimentation in the area of CO oxidation is encouraged in the hope that a consistent picture will emerge regarding the mechanism for this very important reaction. In particular, surface instabilities and self-sustained oscillations should be studied by different investigators under comparable conditions. Reactor geometry, mass and heat transfer effects, fluctuations in gas phase reactant concentrations are important variables which could be minimized by well planned experiments.

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TABLE 1

CO Oxidation Reaction Rates on
Supported Noble Metal Catalysts at 373 K

Catalyst	CO/O_2	TOF molec/site sec X 10^3	EA KJ/mole
Rh/SiO$_2$	0.5	15.3	96
Ru/SiO$_2$	0.5	9.9	90
Pd/SiO$_2$	0.5	0.98	92
Ir/SiO$_2$	0.5	0.60	40
Ru/SiO$_2$	2.0	17.0	100
Ir/SiO$_2$	2.0	3.0	46
Pt/SiO$_2$	2.0	1.53	54
Rh/SiO$_2$	2.0	0.674	110
Pd/SiO$_2$	2.0	0.474	90
Ru/SiO$_2$	4.0	13.2	96
Ir/SiO$_2$	4.0	1.5	40
Pt/SiO$_2$	4.0	1.0	56
Rh/SiO$_2$	4.0	0.5	93
Pd/SiO$_2$	4.0	0.29	102

Oxidizing Conditions   Rh > Ru > Pd > Ir

Reducing Conditions   Ru > Ir > Pt > Rh > Pd

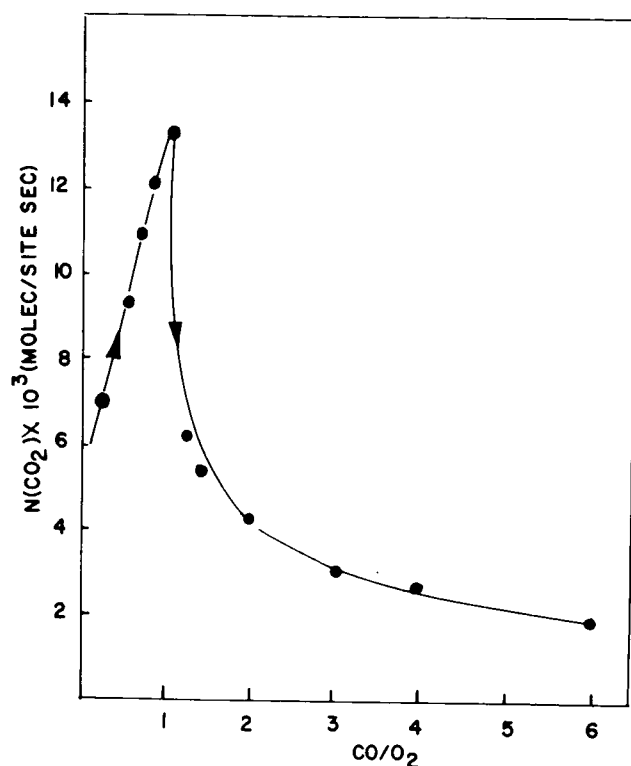Stoichiometric Conditions   Ru > Ir > Pt > Rh > Pd

Fig. 1: *Turnover frequency for CO_2 formation as a function of the CO/O_2 partial pressure ratio at 393 K;* [10]. Copyright 1986 ACS.*
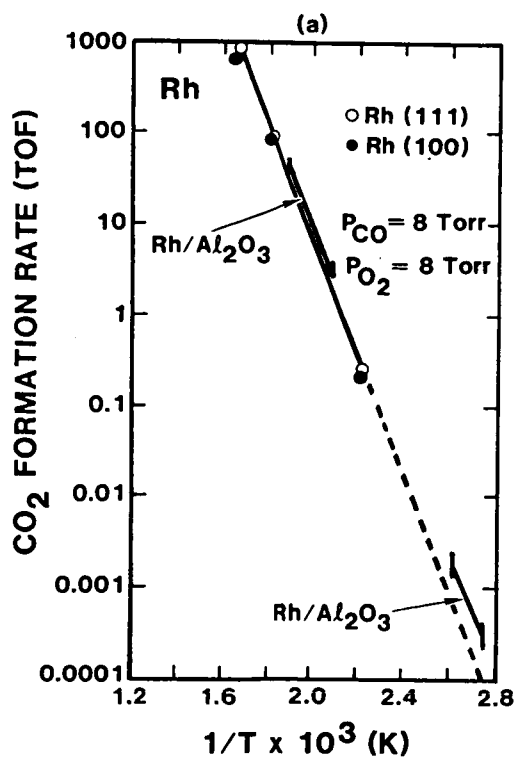

Fig. 2: *Arrhenius Plot CO oxidation on Rh(111), Rh(100) and Rh/Al_2O_3;* reproduced with permission from W. Goodman and J. Peden [20]. Copyright 1986 ACS.*
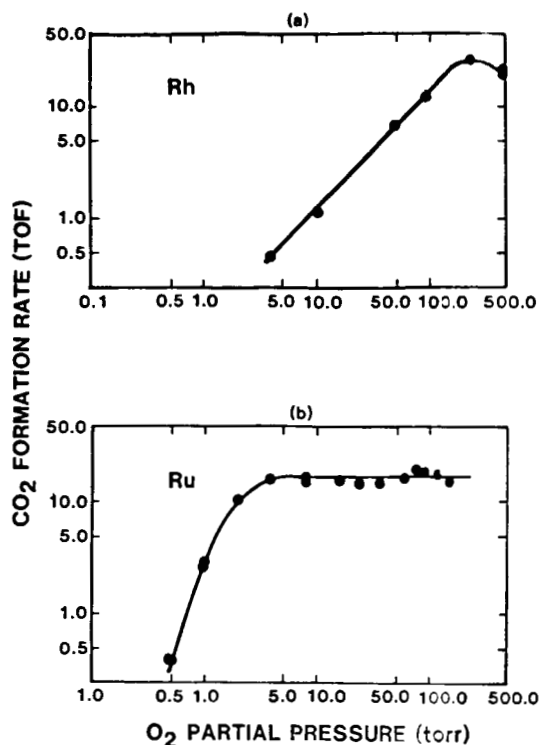
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Fig. 3: *The rate of CO$_2$ formation as a function of oxygen partial pressure; reproduced with permission from W. Goodman and J. Peden [20]. Copyright 1986 ACS.*[*]
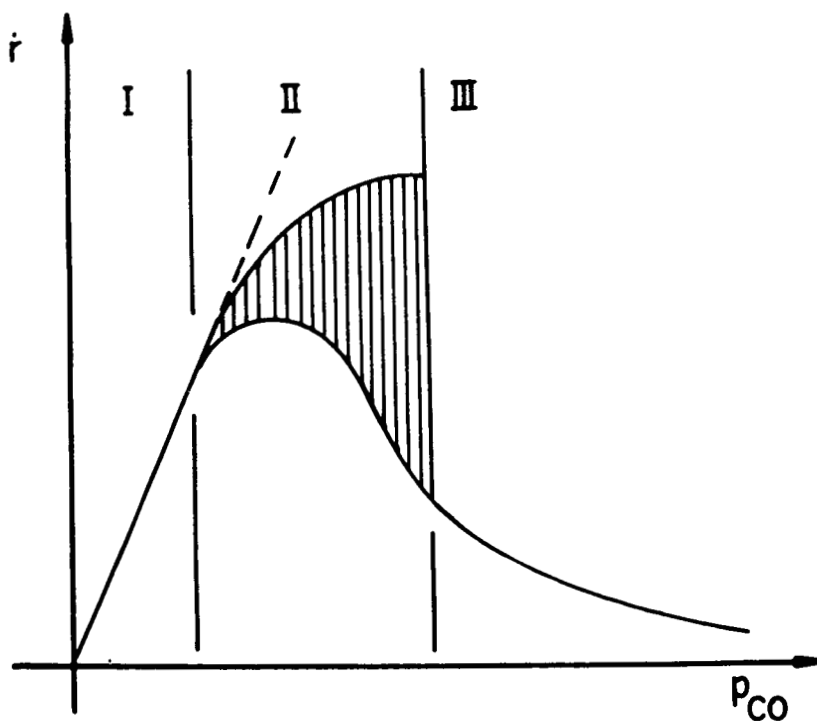
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Fig. 4: *Kinetic regimes which occur during the oxidation of CO; reproduced with permission from E. Wicke et al. [13] Copyright 1980 VCH.*[*]
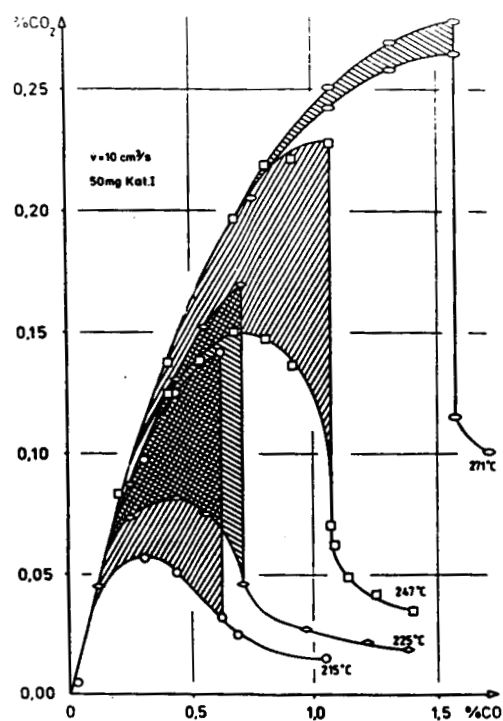
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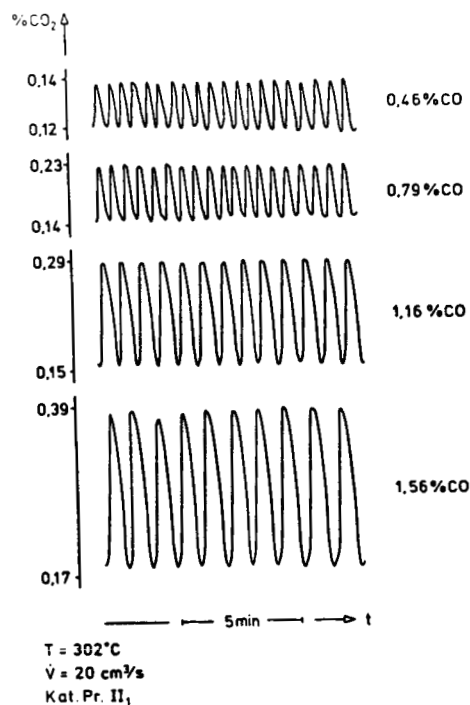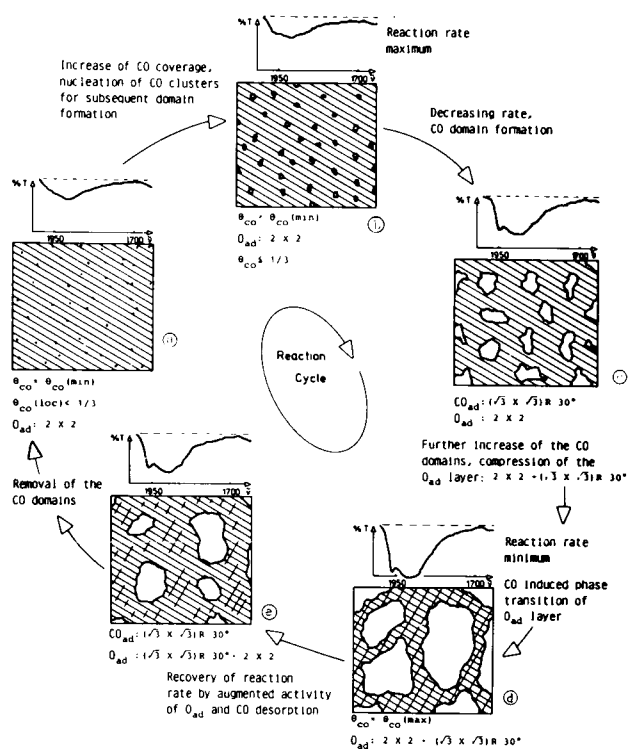Fig. 5: *Regimes of oscillating behavior during the CO
oxidation over Pt/SiO$_2$ [41].*

Fig. 6: *Reaction rate oscillations during the CO oxidation
over Pt/SiO$_2$ [41].*

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Fig. 7: *Self-sustained oscillations obtained by stopping the oxygen programming at 8 cm3/min; (a) CO_2 production, (b) spectragram of adsorbed CO, (c) surface temperature;* reproduced with permission from D. J. Kaul and E. E. Wolf in J.Cat. 91 216-230 (1985).Copyright 1985 ACS.*

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Fig. 8: *Reaction cycle of an oscillation period derived from the IR spectra and supposed structures of chemisorbed layers* [32]. Copyright 1984 Springer-Verlag.